



# Change in photocatalytic NO removal mechanisms of ultrathin BiOBr/BiOI via NO<sub>3</sub><sup>−</sup> adsorption

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## ARTICLE INFO

### Keywords:

NO removal  
Ultrathin structure  
BiOBr/BiOI  
NO<sub>3</sub><sup>−</sup> adsorption  
Photocatalytic mechanism

## ABSTRACT

Improved photocatalytic NO removal of photocatalysts requires enhanced carrier photocatalysis for more reactive species generation. Ultrathin structural BiOBr/BiOI (BiOBr/BiOI-U) photocatalyst was in-situ prepared and it showed enhanced photocatalytic efficiency for NO removal. The underlying photocatalytic process is divided into two steps: in the first step, NO<sub>3</sub><sup>−</sup> was produced in a nonselective oxidation process. The increased NO<sub>3</sub><sup>−</sup> concentration induces NO<sub>3</sub><sup>−</sup> adsorption on the surface oxygen vacancies of the photocatalyst in the second step, which changed the surface environment of the ultrathin BiOBr/BiOI photocatalyst. During this process, the nonselective oxidation process turned into a selective oxidation process with NO<sub>2</sub> as the main product. In addition, the main photogenerated reactive oxygen species contributed to NO removal. Furthermore, the photocatalytic mechanism of BiOBr/BiOI-U was explored.

## 1. Introduction

Currently, global air pollution is the major environmental deterioration. The poor air quality mainly results from pollution with suspended solid particles (PM), nitric oxide (NO), sulfur dioxide (SO<sub>2</sub>), volatile organic compounds (VOCs) and other aromatic hydrocarbons [1]. Among these pollutants, nitric oxide (NO) is mainly produced in fossil energy consumption, which can cause acid rain, photochemical smog and other environmental crises. However, the NO concentration in the atmosphere rose sharply in the past few decades due to the rapid development of transportation and industry. Therefore, development and utilization of green and sustainable strategies for NO removal is urgently necessary. Conventional NO removal technologies are physical adsorption, acid absorption, and alkaline absorption [2–5]. These methods are usually complicated, have high costs, and even cause secondary pollution. Recently, photocatalytic technology has been reported as an efficient alternative strategy for the clean and sustainable NO removal [6]. Upon light illumination, the photocatalysts can generate reactive species, such as photogenerated electrons (e<sup>−</sup>) and holes (h<sup>+</sup>), superoxide (O<sub>2</sub><sup>•−</sup>), singlet oxygen (<sup>1</sup>O<sub>2</sub>) and so on. Through reaction with these photogenerated species, NO can be effectively

removed [7,8].

Bismuth oxyhalide photocatalysts (BiOX, X = Cl, Br, and I), as a new kind of layered oxide semiconductors, have drawn intense attention due to their superior properties under visible light and their potential applications in engineering. In order to further enhance the photocatalytic properties of BiOXs, a series of structurally modified bismuth oxyhalide photocatalysts have been designed and synthesized. Among them, the heterostructural photocatalyst BiOBr/BiOI has been prepared in one pot. The microstructures of heterojunction-containing BiOBr and BiOI with self-similar structures have a considerable influence on their photocatalytic performances [9–13]. The induced carrier separation efficiency and enhanced molecular oxygen activation ability of BiOBr/BiOI have been confirmed in literature [14–17].

In this work, ultrathin BiOBr/BiOI (BiOBr/BiOI-U) photocatalyst with oxygen vacancies was synthesized in situ and applied for NO removal. The ultrathin structure and the surface oxygen vacancies were determined and comprehensively characterized. We observed an enhanced photocatalytic NO removal efficiency for this photocatalyst, and we analyzed the underlying photocatalytic mechanisms of the NO removal. The mechanism change of photocatalytic NO removal via the NO<sub>3</sub><sup>−</sup> adsorption by oxygen vacancies was confirmed. To the best of

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<https://doi.org/10.1016/j.apcatb.2018.10.037>

Received 8 August 2018; Received in revised form 13 September 2018; Accepted 16 October 2018

Available online 19 October 2018

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our knowledge, our study presents the first to use ultrathin BiOBr/BiOI photocatalysts with oxygen vacancies for NO removal. However, only rare studies have been reported on the enhancement of the photocatalytic activity of BiOBr/BiOI.

## 2. Experimental section

### 2.1. Materials preparation

**BiOBr/BiOI-U:** 2 mmol of  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  and 1 mmol of KI were firstly dissolved in 40 mL  $0.1 \text{ mol L}^{-1}$  mannitol solution and then a certain amount of PVP K-30 was dissolved. 40 mL glycol solution containing 1 mmol of KBr was added slowly. After being stirred for 30 min, the result solution was transferred into a 100 mL Teflon-lined stainless steel autoclave and filled up to 80% of the total volume followed by a hydrothermal treatment at  $160^\circ\text{C}$  for 16 h. After the reaction, the precipitate BiOBr/BiOI-U was collected, and washed with deionized water and ethanol several times and then dried at  $60^\circ\text{C}$  in air.

**BiOBr/BiOI:** The same method just used distilled water instead of mannitol solution and without adding PVP K-30.

### 2.2. Characterization

X-ray diffraction (XRD) spectra of the samples operated at room temperature, by a Bruker D8 advance X-ray diffractometer using  $\text{Cu K}\alpha$  radiation and  $2\theta$  scan rate of  $6 \text{ min}^{-1}$ . Diffraction patterns were taken over the  $2\theta$  range  $5\text{--}70^\circ$ . X-ray photoelectron spectroscopy (XPS) measurements were carried out by Thermo Scientific ESCALAB 250XI X-ray Photoelectron Spectrometer (Al  $\text{K}\alpha$ , 150 W, C1s 284.8 eV). UV–vis diffuse reflectance spectra (DRS) were obtained using UV–vis spectra (Perkin Elmer, Lambda 650s,  $\text{BaSO}_4$  as a reference). Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) images were obtained by a JEOL JEM-2100F (RH) Field Emission Electron Microscope.

### 2.3. Reactive oxygen species (ROS) quantification experiments

Nitrotetrazolium blue chloride (NBT,  $2.5 \times 10^{-5} \text{ mol L}^{-1}$ , exhibiting an absorption maximum at 259 nm) and 3,3',5,5'-tetramethylbenzidine (TMB,  $0.1 \text{ g L}^{-1}$ , exhibiting an absorption maximum at 380 nm) were used to determine the photogenerated amount of  $\text{O}_2^{\cdot-}$  and  $^1\text{O}_2$ . NBT ( $2.5 \times 10^{-5} \text{ mol L}^{-1}$ , exhibiting an absorption maximum at 259 nm) and TMB ( $0.1 \text{ g L}^{-1}$ , exhibiting an absorption maximum at 380 nm) were used to determine the amount of photocatalytic  $\text{O}_2^{\cdot-}$  and  $^1\text{O}_2$  generation. 10 mg of photocatalysts were added into 50 mL NBT aqueous and sampling every 10 min; 1 mg of photocatalyst was added 16 mL HAC/NaAc buffer solution ( $\text{pH} = 3.6$ ) and 4 mL distilled water, then 2 mg TMB was added in and sampling every 3 min. Both of them were stirred under a xenon lamp. The production of  $\text{O}_2^{\cdot-}$  was quantitatively analyzed by detecting the concentration of NBT and  $^1\text{O}_2$  was analyzed by the oxidation rate of TMB with a UV–vis spectrophotometer.

### 2.4. ESR tests

50  $\mu\text{L}$  of aqueous suspension of samples ( $2 \text{ mg L}^{-1}$ ) was characterized using a Bruker EMX plus model spectrometer operating at the X-band frequency (9.4 GHz) at room temperature for  $^1\text{O}_2$ ,  $\text{O}_2^{\cdot-}$  and oxygen vacancies test directly with a xenon lamp (50 W) as the light source.

### 2.5. Photocatalytic NO removal

The photocatalytic experiments of NO removal at ppb levels were performed at ambient temperature in a continuous flow reactor. The volume of the rectangular reactor, which was made of stainless steel

and covered with quartz glass, was 4.5 L ( $30 \text{ cm} \times 15 \text{ cm} \times 10 \text{ cm}$  [ $\text{L} \times \text{W} \times \text{H}$ ]). One sample dish containing the sample film was placed in the middle of the reactor. An Xe lamp ( $\lambda > 420 \text{ nm}$ ) was used as the visible light source. 0.15 g of photocatalyst was added into 15 mL of  $\text{H}_2\text{O}$  and ultrasonicated for 20 min. The aqueous suspension was then coated onto the glass dish, which was then dried at  $60^\circ\text{C}$  until water was completely removed. NO gas was obtained from a compressed gas cylinder at a concentration of NO with traceable National Institute of Standards and Technology specifications. After adsorption–desorption equilibrium among gases and photocatalysts were achieved, the lamp was turned on. The concentration of NO was continuously measured using a chemiluminescence NO analyzer.

### 2.6. Photoelectrochemical measurement

Electrochemical impedance spectra (EIS) and transient photocurrent responses of the prepared samples were tested by a CHI660D electrochemical working station (CHI Instruments, Shanghai, China) in a three-electrode quartz cell with  $\text{Na}_2\text{SO}_4$  ( $0.1 \text{ mol L}^{-1}$ ) electrolyte solution. Samples were deposited on a fluorinated-tin-oxide (FTO) conducting glass as the working electrode, Ag/AgCl and Pt were used as the reference and the counter electrodes, respectively.

### 2.7. Trapping experiments

**Trapping experiments for photocatalytic NO removal:** for detecting the active species during photocatalytic reactivity, singlet oxygen ( $^1\text{O}_2$ ), superoxide radical ( $\text{O}_2^{\cdot-}$ ) and electron ( $\text{e}^-$ ) were investigated by adding 2 mmol 2,2,6,6-tetramethylpiperidine nitrogen oxide (TEMPO, a quencher of  $^1\text{O}_2$ ), benzoquinone (BQ, a quencher of  $\text{O}_2^{\cdot-}$ ) and  $\text{AgNO}_3$  (a quencher of  $\text{e}^-$ ), respectively.

**Trapping experiments for exploration of singlet oxygen generation:** ESR for singlet oxygen ( $^1\text{O}_2$ ) were tested without any quencher, adding 2 mmol TEMPO (a quencher of  $^1\text{O}_2$ ) and BQ (a quencher of  $\text{O}_2^{\cdot-}$ ), respectively.

## 3. Results and discussion

X-ray diffraction (XRD) patterns were firstly used to confirm the characteristic diffraction peaks of the as-prepared samples. As shown in Fig. 1a, the characteristic peaks of BiOBr and BiOI were in agreement with reported values (BiOI: PDF: 01-073-2062; BiOBr: PDF: 01-078-0348) [18,19]. As for the heterostructural photocatalysts, they contained all the characteristic peaks of the constituent monomers, which indicated that the coupling of BiOBr and BiOI was successful. Compared with BiOI, the flattened and broadened diffraction peaks of BiOBr/BiOI-U were one of the characteristic features of this ultrathin photocatalyst [20]. Fig. 1b and c showed the morphologies of the as-prepared samples. BiOBr/BiOI-U exhibited uniform, homogeneous, and the smaller flaky BiOI was coupled with BiOBr nanosheets. In contrast, BiOBr/BiOI formed a larger, massive structure. The heterostructures of these two samples were clearly resolved by HRTEM. Fig. 1d and e showed the enlarged ultrathin structure BiOBr/BiOI-U at b1 and b2. Fig. 1d demonstrated that the interlayer distance of the {110} facets in BiOBr were 0.276 nm. Fig. 1e showed that the distance of the {001} facets of BiOI-U was 0.950 nm, which was larger than the distance of 0.915 nm of standard BiOI sample according to a previous report [21]. Fig. 1f, and g were c1 part of Fig. 1c, revealing BiOBr in BiOBr/BiOI. It also demonstrated that the interlayer distance of the {110} facets in BiOBr were 0.276 nm. Selected area electron diffraction (SAED) patterns (Fig. 1g) showed rectangular diffraction points. The angle between {110} and {200} facets was  $45^\circ$ , and the angle between {110} and {1-10} facets was  $90^\circ$ , which was in agreement with previous reports [22]. Fig. 1h and i were c2 part of Fig. 1c. The distance of the {110} facets of BiOI was 0.284 nm, and (SAED) patterns (Fig. 1i) also showed rectangular diffraction points. The angle between {110} and {200}

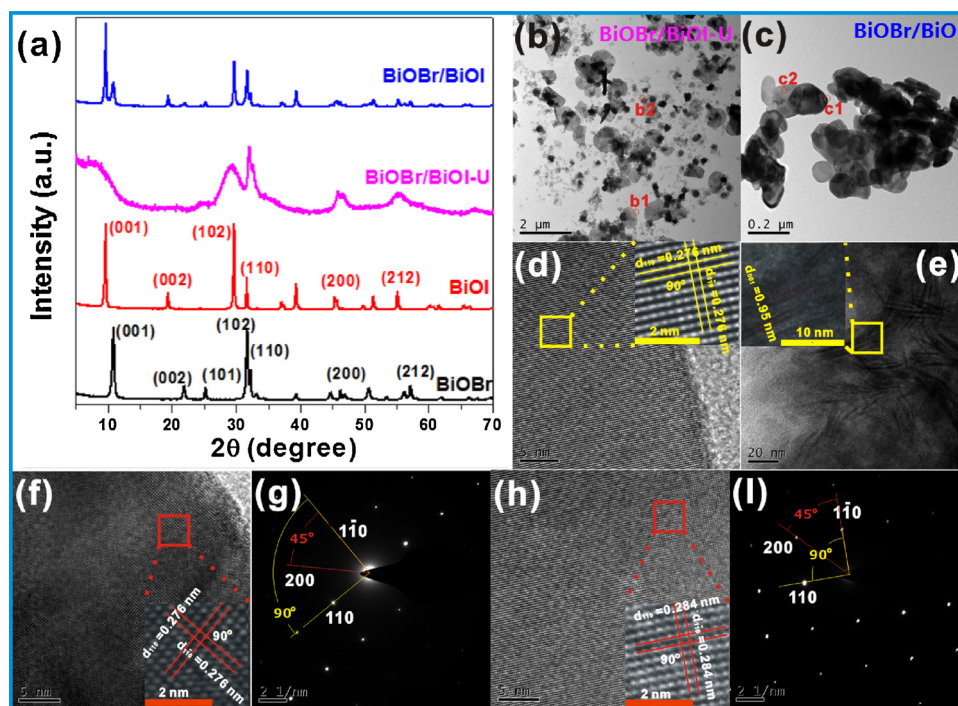


Fig. 1. XRD patterns of BiOBr/BiOI and BiOBr/BiOI-U (a); TEM and HRTEM patterns of BiOBr/BiOI-U (b), (d), (e); TEM and HRTEM patterns of BiOBr/BiOI (c), (f) and (h); and SAED patterns of BiOBr/BiOI (g) and (i).

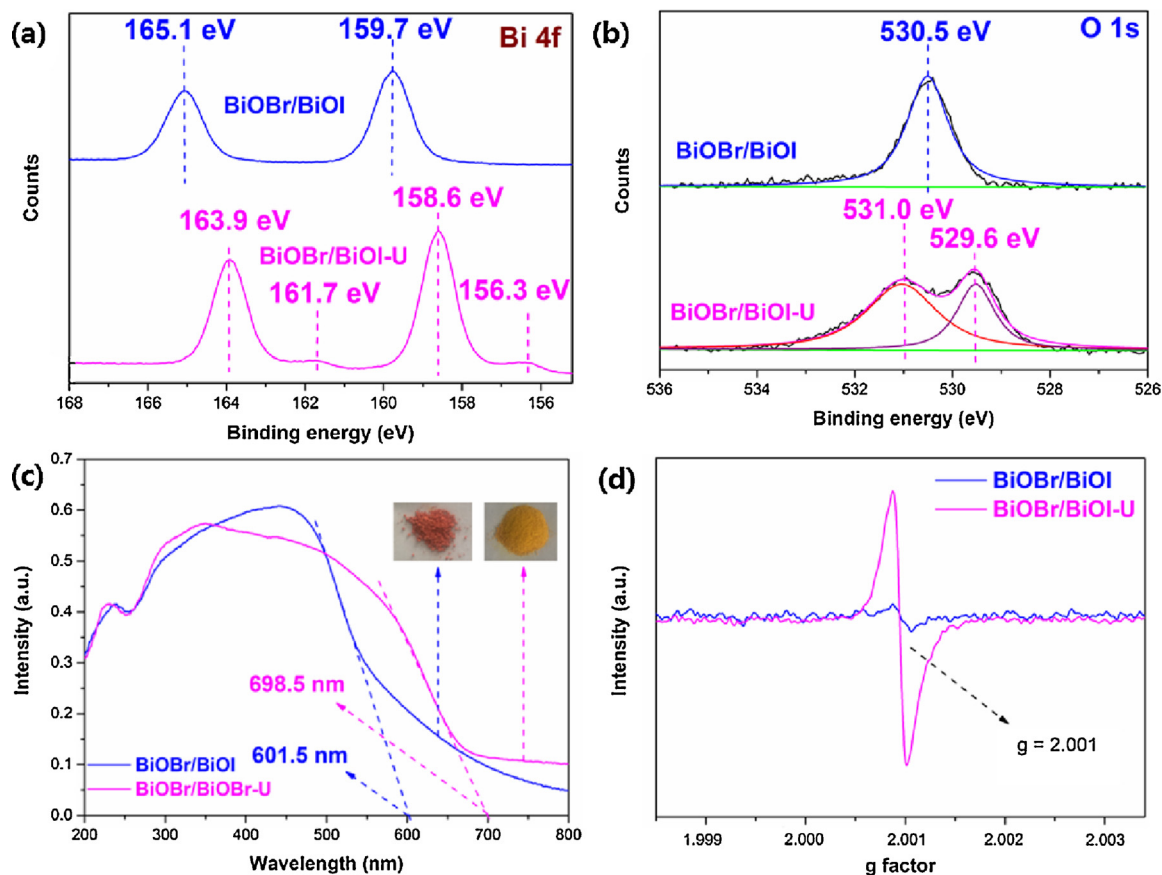
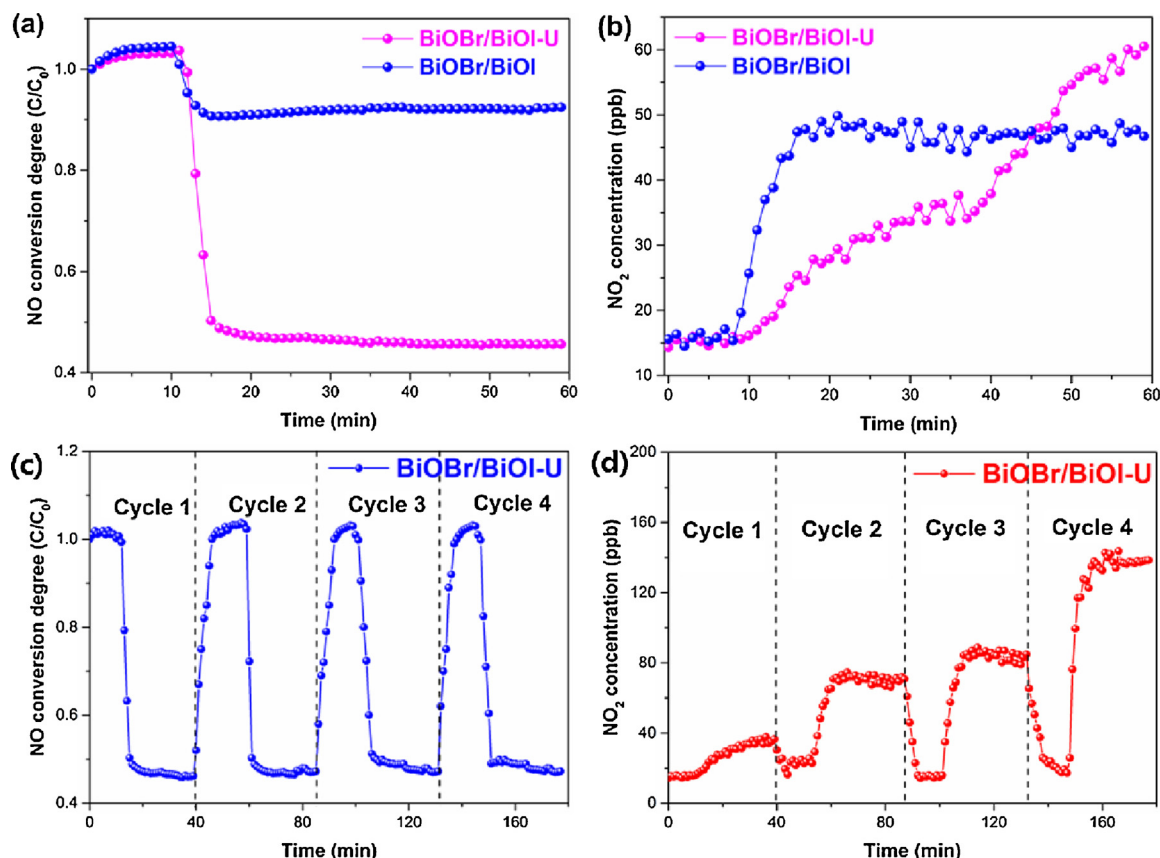


Fig. 2. XPS patterns of Bi 4f (a) and O 1s (b); DRS patterns (c) and EPR (d) of BiOBr/BiOI and BiOBr/BiOI-U.



**Fig. 3.** Comparison of the photocatalytic NO removal of BiOBr/BiOI and BiOBr/BiOI-U (a); NO<sub>2</sub> generation on BiOBr/BiOI and BiOBr/BiOI-U (b); stability of BiOBr/BiOI-U in multiple NO removal cycles (c); and change of the NO<sub>2</sub> concentration with the increasing number of cycles (d).

facets was 45°, and the angle between {110} and {1–10} facets was 90°, which was in agreement with previous reports about BiOI [18,21]. **Figure S1** showed the N<sub>2</sub> adsorption and desorption curves of these two samples, which were all type-IV adsorption isotherms [23]. In addition, the hysteresis loops in the adsorption isotherms indicated that BiOBr/BiOI-U and BiOBr/BiOI exhibited mesoporous structures. The specific surface area of BiOBr/BiOI-U was 25.59 m<sup>2</sup> g<sup>−1</sup>, which was larger than the specific surface area of 11.56 m<sup>2</sup> g<sup>−1</sup> of BiOBr/BiOI. The expanded specific surface area of BiOBr/BiOI-U was caused by its ultrathin structure. The **Figure S1** inset showed the pore distribution curves; the peak at 3.54 nm was equaled with the distance between the nanoscales of BiOBr/BiOI-U, which was much narrower than the distance of 25.99 nm determined for BiOBr/BiOI. BET analysis also demonstrated that the enlarged specific surface area of BiOBr/BiOI-U was due to its ultrathin structure.

The elemental compositions of the surfaces were investigated by X-ray photoelectron spectroscopy (XPS; **Figure S2a**), demonstrating that the surfaces of these two samples consisted of the same elements of Bi, O, Br, and I. **Fig. 2a** showed that the Bi 4f binding energies of BiOBr/BiOI were values of 165.1 and 159.7 eV. Compared with BiOBr/BiOI, BiOBr/BiOI-U moved toward larger binding energies of 163.9 and 158.6 eV, indicating the appearance of Bi<sup>3+</sup>. This phenomenon might be due to the generation of oxygen vacancies according to a previous report, [24]. And the oxygen vacancies also supported by the two XPS peaks BiOBr/BiOI-U exhibited at 161.7 and 156.3 eV, which were typical for the formation of oxygen vacancies [21,25]. The O 1s peak at 530.5 eV (**Fig. 2b**) was assigned to the Bi–O bonds of BiOBr/BiOI. Besides the typical Bi–O bonds at 529.6 eV, BiOBr/BiOI-U showed a peak at 531.0 eV that implied the absence of crystal lattice oxygen [26,27]. **Figure S2b** and **S2c** showed the binding energies of BiOBr/BiOI were at 631.1 and 619.6 eV and of BiOBr/BiOI-U were at 630.1 and

618.6 eV, which could be assigned to I 3/2 and I 5/2, respectively. The Br 3d binding energies of BiOBr/BiOI and BiOBr/BiOI-U were at 68.95 and 68.10 eV, respectively. UV–vis diffuse reflectance spectroscopy (DRS) was performed for comparing the maximum absorption wavelength. As shown in **Fig. 2c**, BiOBr/BiOI-U had a higher visible light absorption than BiOBr/BiOI. This characterization presented an induced property and might be due to the oxygen vacancies according to previous reports [26]. Two pictures inset in **Fig. 2c** showed that BiOBr/BiOI and BiOBr/BiOI-U were red and dark yellow, respectively. EPR is considered to provide direct evidence of oxygen vacancy formation, and the observed stronger signal implies generation of more oxygen vacancies [28]. In **Fig. 2d**, both BiOBr/BiOI and BiOBr/BiOI-U showed signals at g = 2.001, which were typical for oxygen vacancies [29]. The much stronger signal of BiOBr/BiOI-U indicated that more oxygen vacancies were generated in its bulk structure, which was in agreement with DRS and XPS results.

BiOBr/BiOI-U and BiOBr/BiOI were applied for photocatalytic NO removal in air. Before visible light irradiation, adsorption/desorption equilibrium between gas and samples was reached. After 10 min adsorption, NO removal was initiated on the photocatalysts. **Fig. 3a** showed changes in the NO concentration (C/C<sub>0</sub>) after visible light irradiation for 50 min in the presence of BiOBr/BiOI-U or BiOBr/BiOI. After visible light irradiation of BiOBr/BiOI-U and BiOBr/BiOI was started, the NO concentration started to decrease. We observed that the NO concentration decrease was stronger expressed on BiOBr/BiOI-U than on BiOBr/BiOI. This conclusion was drawn as BiOBr/BiOI-U efficiently removed about 57% of NO by decreasing the concentration from around 600 ppb (C/C<sub>0</sub> = 1) to around 258 ppb (C/C<sub>0</sub> = 0.43), while BiOBr/BiOI removed only about 10% of NO in 50 min. These outstanding NO removal properties of BiOBr/BiOI-U were due to enhanced carrier photocatalysis, which was also verified by molecular oxygen



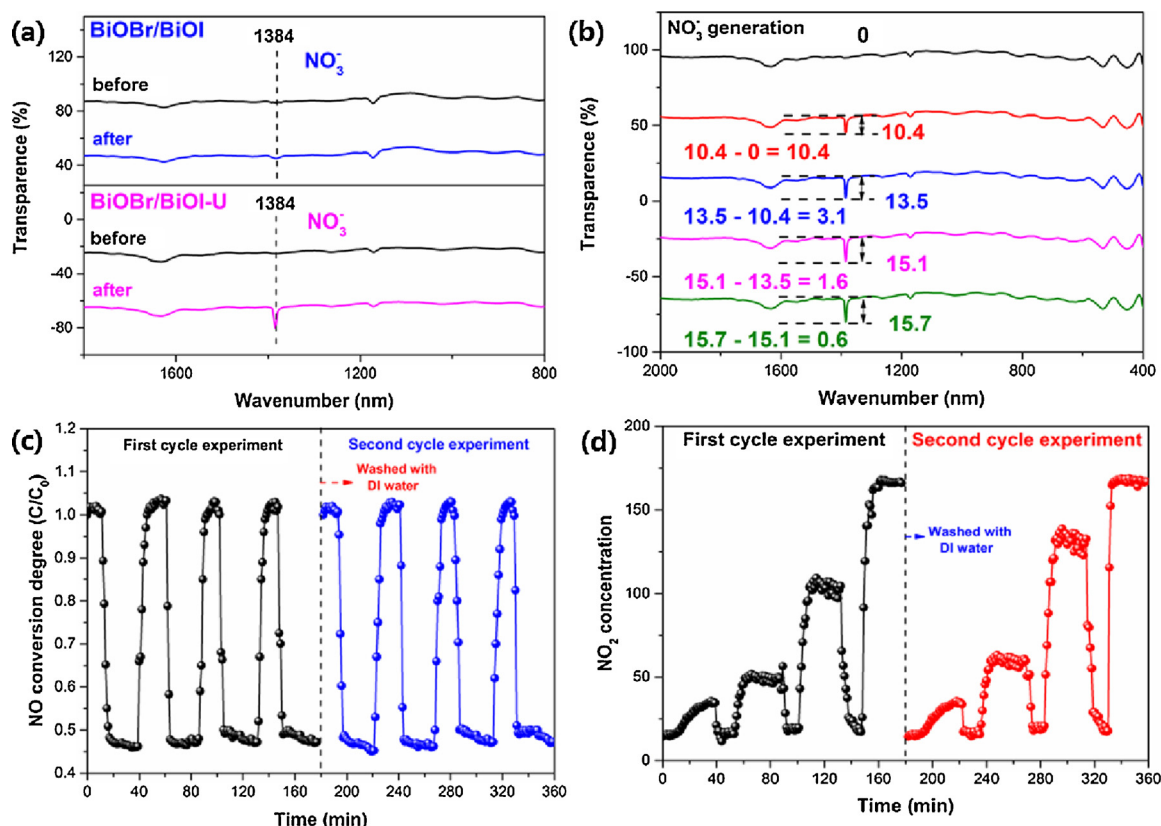


Fig. 4. Original FT-IR patterns (a) and FT-IR patterns after each cycle (b) of BiOBr/BiOI-U; stability of BiOBr/BiOI-U in multiple NO removal cycles before and after washing with deionized (DI) water (c); and change of the  $\text{NO}_2$  concentration with increasing cycle number before and after washing with DI water (d).

activation ability, [30,31] equivalent series resistance (ESR; Figure S3), photoluminescence (PL; Figure S4), [32] electrochemical impedance spectroscopy (EIS; Figure S5), [33] transient photocurrent responses (TPR; Figure S6), [34] and ESR trapping experiments (Figure S7) [35]. In addition, we also measured the change of the  $\text{NO}_2$  concentration during the whole NO removal process (Fig. 3b). For BiOBr/BiOI-U, we observed that a small amount of  $\text{NO}_2$  was produced in the beginning of the NO removal process. This phenomenon demonstrated that NO oxidation induced by BiOBr/BiOI-U was nonselective, and most NO was oxidized to  $\text{NO}_3^-$  [36]. With increasing time, the concentration of  $\text{NO}_2$  produced by BiOBr/BiOI-U increased sharply, while that produced by BiOBr/BiOI remained constant. Otherwise, to test the stability of BiOBr/BiOI-U for NO removal, we reused the BiOBr/BiOI-U photocatalyst for four cycles under the same experimental conditions, as shown in Fig. 3c. The photocatalytic NO removal efficiency of BiOBr/BiOI-U did not decline during these four cycles, indicating that BiOBr/BiOI-U was stable and sustainable in the photocatalytic removal of NO. However, Fig. 3d showed that the amount of generated  $\text{NO}_2$  increased after each cycle. According to previous reports, [37]  $\text{NO}_3^-$  was expected to be the final product of the nonselective oxidation of the NO removal process, while  $\text{NO}_2$  was expected to be the product of the corresponding selective oxidation process. [38] The increased  $\text{NO}_2$  concentration (Fig. 3b,d) implied that the nonselective oxidation process might be changed into the selective oxidation process.

In order to further confirm the superior NO removal efficiency of BiOBr/BiOI-U, the amount of produced  $\text{NO}_3^-$  was detected by Fourier transform infrared spectroscopy (FT-IR; Fig. 4a). The peak at 1384 nm was the typical  $\text{NO}_3^-$  signal, [39,40] and we found that its intensity was stronger on BiOBr/BiOI-U than on BiOBr/BiOI, which was in agreement with the NO removal results. To analyze the reason for the change from nonselective to selective oxidation process, we first compared the XRD patterns (Figure S8) of original and used BiOBr/BiOI-U (after four

cycles), which did not show any obvious changes in the crystalline structure of BiOBr/BiOI-U. This finding confirmed that the change in the NO removal mechanism was not accompanied by any structural changes of BiOBr/BiOI-U. In order to confirm that  $\text{NO}_3^-$  was generated in the nonselective oxidation process and influenced the photocatalytic NO removal, the produced  $\text{NO}_3^-$  was measured by FT-IR after each cycle. Although the  $\text{NO}_3^-$  concentration continuously increased, the concentration increment became clearly smaller after each cycle, which was from 10.4 of the 1st cycle to 3.1 of the 2nd, then to 1.6 of the 3rd cycle and 0.6 of final cycle. The sharp decrease of the  $\text{NO}_3^-$  increment (from 10.4 to 3.1) indicated that ultrathin BiOBr/BiOI-U could adsorb more  $\text{NO}_3^-$ . Oxygen vacancies on the bulk of the photocatalysts could enhance the adsorption capacity. Herein, to confirm the specific adsorption of the  $\text{NO}_3^-$ , EPR was used to detect signal intensity of the oxygen vacancies before and after cyclic experiments. As was shown in Figure S9, the obvious signal decrease could be explained by the  $\text{NO}_3^-$  adsorption. The weak signal of the oxygen vacancies after the cyclic experiment implied that  $\text{NO}_3^-$  was adsorbed on the oxygen vacancies on the bulk of the BiOBr/BiOI-U. The  $\text{NO}_3^-$  adsorption affected the concentration of oxygen vacancies and changed the photocatalytic mechanism of the NO removal. Above experimental results demonstrated that  $\text{NO}_3^-$  generated in the nonselective oxidation adsorbed on the oxygen vacancies of the BiOBr/BiOI-U and changed the photocatalytic NO removal into a selective oxidation process, which also explained the increased  $\text{NO}_2$  concentration. In order to further confirm the influence of  $\text{NO}_3^-$ , we entirely washed off  $\text{NO}_3^-$  from the BiOBr/BiOI-U photocatalyst using DI water after four cycles and started a new NO removal cyclic experiment. The photocatalyst remained stable for photocatalytic NO removal under visible light irradiation both before and after washing off  $\text{NO}_3^-$  (Fig. 4c). In contrast, the  $\text{NO}_2$  generation increased, which was in agreement with previous results (Fig. 4d). However, when the BiOBr/BiOI-U photocatalyst was washed with DI

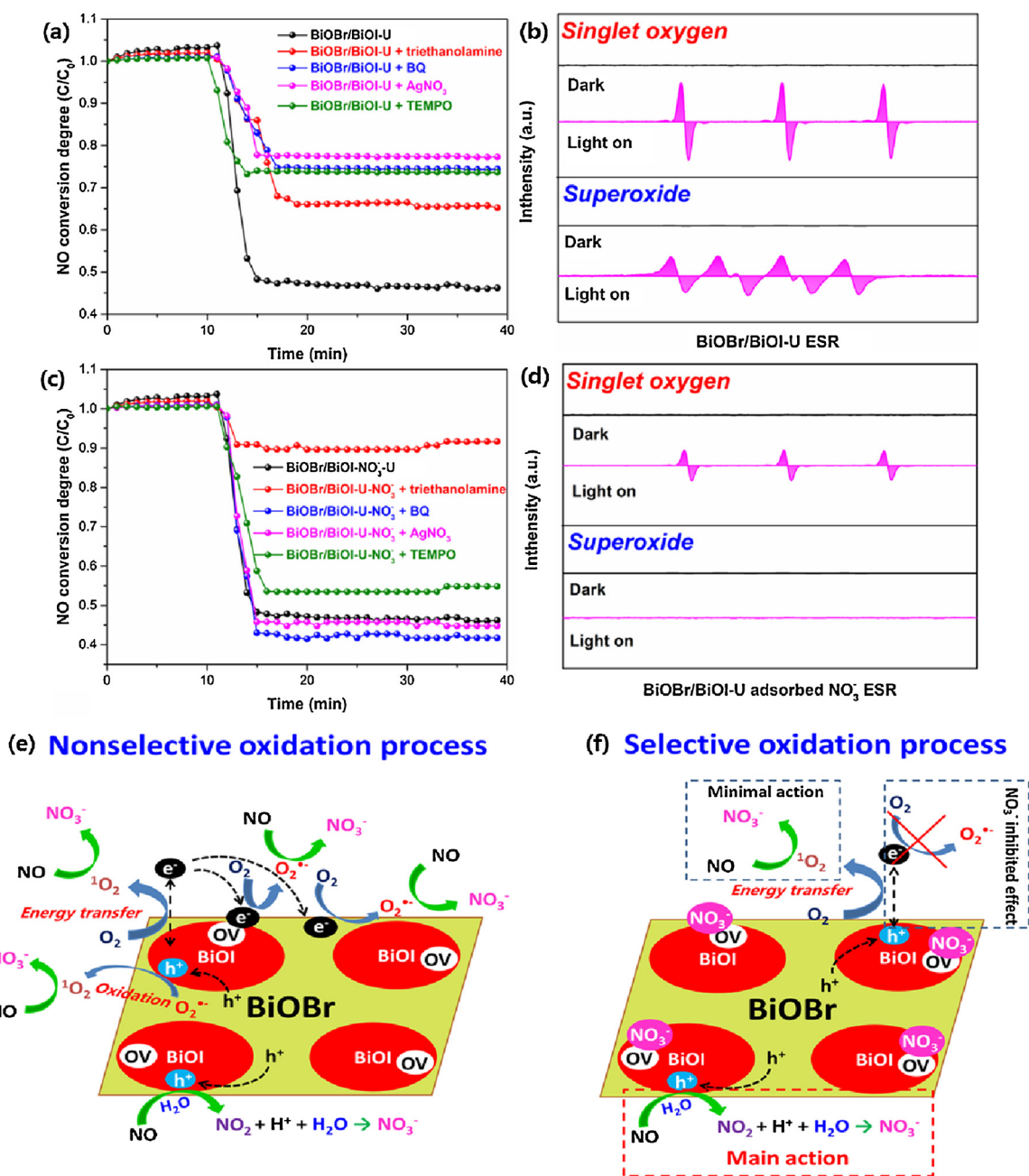
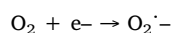
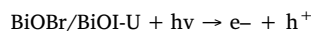


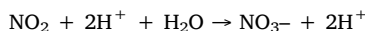
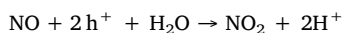
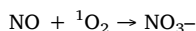
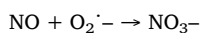
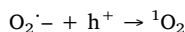
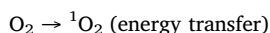
Fig. 5. Comparison of photocatalytic activities of BiOBr/BiOI-U with different trapping agents under visible light irradiation (a); ESR test for <sup>1</sup>O<sub>2</sub> and O<sub>2</sub><sup>•-</sup> in dark and light on (b); comparison of photocatalytic activities of BiOBr/BiOI-U after NO<sub>3</sub><sup>-</sup> adsorption with different trapping agents under visible light irradiation (c); ESR test for <sup>1</sup>O<sub>2</sub> and O<sub>2</sub><sup>•-</sup> in dark and light on (d). NO removal mechanisms of BiOBr/BiOI-U (e) and (f).

water, the NO<sub>2</sub> amount was notably small and slowly decreased to the original increased amount, which was in agreement with the amount before washing. We concluded that the photocatalytic NO removal process was reverted after NO<sub>3</sub><sup>-</sup> was washed from the surface oxygen vacancies of the BiOBr/BiOI-U photocatalyst. Therefore, the change of the photocatalytic NO removal process from nonselective to selective oxidation was due to the adsorption of photogenerated NO<sub>3</sub><sup>-</sup> on the surface oxygen vacancies of BiOBr/BiOI-U.

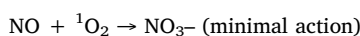
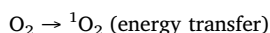
NO removal processes with different trapping agents were studied to elucidate the photocatalytic mechanism. Triethanolamine, benzoquinone, AgNO<sub>3</sub>, and tetramethyl piperidine nitrogen oxide (TEMPO) were used for trapping photogenerated holes, O<sub>2</sub><sup>•-</sup>, electrons, and <sup>1</sup>O<sub>2</sub>. Fig. 5a showed the trapping results of the nonselective process of the NO removal. Compared with NO removal without any trapping agent, the concentration of NO obviously decreased after adding any of these

trapping agents, indicating that the photogenerated electrons, holes, O<sub>2</sub><sup>•-</sup>, and <sup>1</sup>O<sub>2</sub> were all efficient for NO removal. ESR also proved that BiOBr/BiOI-U effectively generated O<sub>2</sub><sup>•-</sup> and <sup>1</sup>O<sub>2</sub> (Fig. 5b). In combination with previous results, we proposed that photogenerated electrons contribute to the generation of O<sub>2</sub><sup>•-</sup>. Meanwhile, the oxygen vacancies in the bulk of the BiOBr/BiOI-U photocatalyst were also optimal for O<sub>2</sub><sup>•-</sup> to capture electrons. <sup>1</sup>O<sub>2</sub> was generated by both energy transfer and reaction of O<sub>2</sub><sup>•-</sup> with holes. All these processes promoted the NO removal. In combination with experimental results and previous studies, the nonselective NO removal process could be formulated as follows and illustrated in Fig. 5e: [41,42]





We also explored the photocatalytic mechanism of the NO removal for the BiOBr/BiOI-U photocatalyst after  $\text{NO}_3^-$  adsorption. Herein, we used the catalyst obtained after the cyclic experiment for the trapping experiments, and the corresponding results were shown in Fig. 5c. After adding benzoquinone and  $\text{AgNO}_3$ , BiOBr/BiOI-U remained its original properties for NO removal, suggesting that photogenerated electrons and  $\text{O}_2^{\cdot-}$  did not contribute to the NO removal. While the obvious decline after using triethanolamine and TEMPO indicated that the main reactive species for NO removal were photogenerated holes and  ${}^1\text{O}_2$ , this mechanism was different from that of BiOBr/BiOI-U before  $\text{NO}_3^-$  adsorption. According to previous reports,  $\text{NO}_3^-$  adsorption changed the photocatalyst surface to inhibit the generation of reactive oxygen species. The  $\text{NO}_3^-$  adsorption cripples the trapped electron capacity of the oxygen vacancies. To confirm this conclusion, we also measured ROSs of BiOBr/BiOI after  $\text{NO}_3^-$  adsorption by ESR spectra. No  $\text{O}_2^{\cdot-}$  peaks could be detected in the aqueous dispersions both in dark and light on, confirming that  $\text{NO}_3^-$  generated during the NO removal process inhibited the generation of  $\text{O}_2^{\cdot-}$ , while the weak  ${}^1\text{O}_2$  signal proved that  ${}^1\text{O}_2$  was only generated by energy transfer rather than reaction of  $\text{O}_2^{\cdot-}$  with holes. Therefore, the presence of oxygen vacancies leded  $\text{NO}_3^-$  adsorption, and the photocatalytic mechanisms of NO removal were changed from the nonselective oxidation process into selective oxidation process with a large number of  $\text{NO}_2$  generation during this process. The whole process was illustrated in the following and in Fig. 5f: [43,44]



#### 4. Conclusion

In conclusion, the enhanced photocatalytic activity for NO removal of BiOBr/BiOI-U photocatalyst has been showed. Through the XRD, HRTEM and other efficient characterizations, the ultrathin structure and oxygen vacancies of BiOBr/BiOI-U were determined. The mechanism study revealed that the whole photocatalytic NO removal process was divided into two parts: nonselective oxidation process firstly occurred and  $\text{NO}_3^-$  was the main product in this period. The adsorbed  $\text{NO}_3^-$  on oxygen vacancies of the BiOBr/BiOI-U changed the photocatalytic NO removal mechanism from nonselective oxidation process to selective oxidation process which induced  $\text{NO}_2$  generation. The surface oxygen vacancies of BiOBr/BiOI-U was the key factor for the photocatalytic NO removal mechanism change.

#### Acknowledgment

This work was supported by the National Natural Science Foundation of China (No. 51872147, 51502146, 51702270, 21671113), the Program for Innovative Research Team of Science and Technology in the University of Henan Province (19IRTSTHN025) and Petro China Innovation Foundation (2018D-5007-0604).

#### Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:<https://doi.org/10.1016/j.apcatb.2018.10.037>.

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